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14. ABSTRACT
As part of an ongoing investigation into the effect of plasma treatment on permethrin adhesion to Army Combat Uniform fabric, a new desorption-gas chromatography–mass spectrometry based screening tool for permethrin content in military fabrics was developed. The method allows for the direct analysis of fibers without the use of solvent extraction, making the method both quicker and greener as compared with the current standard method of analysis. While the method was demonstrated for permethrin only, it is expected to be applicable to other treatments as well.

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1. Background/Introduction

Permethrin content in military fabrics is measured at the factory and at government laboratories where it is determined using a complicated and labor-intensive test. The quantification method is from Military Specification GL/PD 07-13A[1] and GL/PD 07-14A (Army),[2] and from MIL-PRF-MCCUU E (Marine Corps Combat Utility Uniform).[3] Samples are cut from various areas of a treated uniform, and the permethrin contained in the specimens is extracted with solvent with a recovery rate of at least 95%. Samples are analyzed using a gas chromatograph–mass spectrometer (GC-MS), and peak areas are compared with calibration curves to quantify the amount of permethrin. A series of external standards is used to generate a calibration curve for permethrin concentration. Individual uniforms are tested initially (before laundering) and after a specified number of laundering cycles, in accordance with the American Association of Textile Chemists and Colorists (AATCC) laundering standard AATCC 135, 3, V, Aiii.[4]

As part of an ongoing investigation into the effect of plasma treatment on permethrin adhesion to Army Combat Uniform (ACU) fabric, a new desorption-GC-MS (D-GS-MS)-based screening tool for permethrin content in military fabrics was developed. The method allows for the direct analysis of fibers without the use of solvent extraction, making the method both quicker and greener as compared with the current standard method of analysis. While the method was demonstrated for permethrin only, it is expected to be applicable to other treatments as well.

2. Experimental

The factory treated and laboratory treated fabrics used in this study were prepared using commercial formulations of permethrin. These are usually a blend of active ingredient, solvent, and surfactants. For the laboratory-prepared samples, the concentrate Permethrin SFR (Martin's, Pasadena, TX) was used, containing 36.8% permethrin with a *cis/trans* ratio of approximately 42/58%. The concentrate is used in a 1:100 dilution ratio with water, and for laboratory finishing, is applied to the fabric using a syringe with a known amount of solution. The concentrate is a clear yellow color with an oily appearance; however, when diluted with water it instantly forms a milky suspension that is opaque and less viscous than the concentrate.

The cloth used in this investigation included factory and laboratory-prepared permethrin-treated uniform fabric. In all cases, the ACU fabric was a 50/50 blend of cotton and nylon (NyCo) in a ripstop weave with a printed Operational Camouflage Pattern (OCP). The maximum application rate of permethrin as an

impregnated material onto fabric used for personal or military clothing is set by the US Environmental Protection Agency (EPA) as 0.125 mg/cm^2. This is found in the Reregistration Eligibility Decision (RED) for Permethrin, EPA 738-R-09-306, May 2009.[5] For NyCo, this is equivalent to 0.52% w/w. The permethrin formulation contains approximately 40% permethrin in a petroleum distillate emulsion.

A standard solution containing a known amount of permethrin was prepared using the solid form of permethrin purchased from Sigma-Aldrich, which is composed of *cis* and *trans* isomers. An amount weighing 1.37 mg was dissolved in 0.5 mL of ethanol. A calibration curve was generated by analyzing 1, 2, and 3 uL of the solution and plotting areas of the selected ion chromatograms (SICs) for m/z = 183 against the known concentration.

Desorption and pyrolysis products were analyzed by means of D-GC-MS. Desorption was achieved via a CDS Analytical Model 2000 Pyroprobe (coil type) connected through a heated interface chamber to the splitless injector of an Agilent (Santa Clara, CA) GC-MS system (Model 6890N GC and Model 5973N MSD). The GC column used was a HP-5 capillary column (0.25 mm × 30 m, 0.25-μm film). The injector temperature was 200 °C; the Pyroprobe interface was set to a temperature of 250 °C. The GC oven temperature program was as follows: 100 °C isothermal for 1 min, 100–250 °C at 40 °C/min, and 250 °C isothermal for 1 min. The Pyroprobe was programmed to give a 20-s desorption pulse at 250 °C at a heating rate of 1,000 °C/s. The pulse temperature is based on calibration provided by the vendor and was not measured for this study. Samples (1–2 mg) were held within the coil of the Pyroprobe by first placing them in a quartz tube containing a small plug of glass wool, and then inserting the entire tube into the coil. Selected ion chromatograms (SICs) were obtained via Hewlett Packard ChemStation software by extracting specified masses from the total ion chromatogram (TIC). The major fragment ion of permethrin at *m/z* 183 was used for quantification. The peak area was integrated for each isomer and added together to give a total count for the specific amount of permethrin in the injected specimen.

3. Results

Figure 1 shows the TIC (m/z =183) for the permethrin standard. Permethrin has a retention time of just under 10 min. The *cis* and the *trans* isomers are represented by separate peaks; *cis* is first, then *trans*.

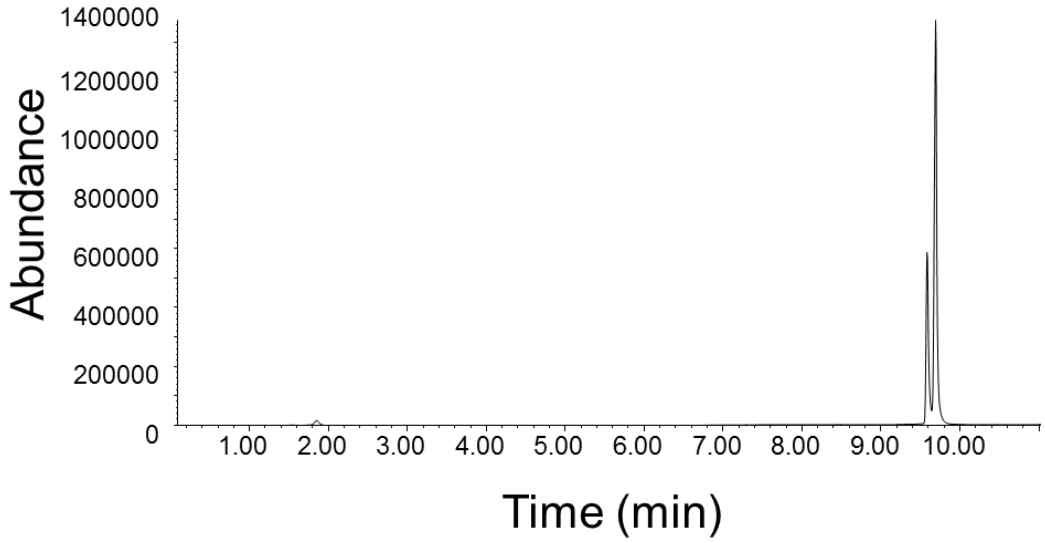

Fig. 1 TIC for permethrin standard in ethanol

Three different injections of 1, 2, and 3 µL of the standard solution used to generate the calibration curve are shown in Fig. 2.

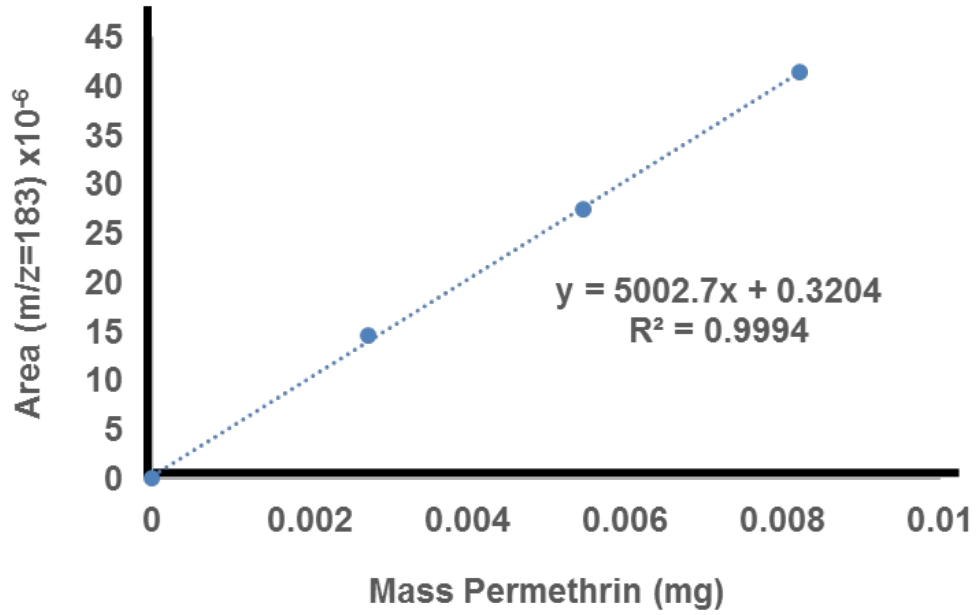

Fig. 2 Calibration curve using permethrin standard solution (in ethanol)

For the fabric specimens, fibers were pulled from different areas of a treated or untreated fabric. Figure 3 shows the TIC for NyCo fibers taken from a permethrin-treated uniform fabric that has been factory finished (FF). The peak near 1.2 min is an experimental artifact that results from the introduction of air into the system when the Pyroprobe is inserted in the GC interface. As was observed for the

standard material, desorbed *cis* and *trans* permethrin isomers eluted at just under 10 min.

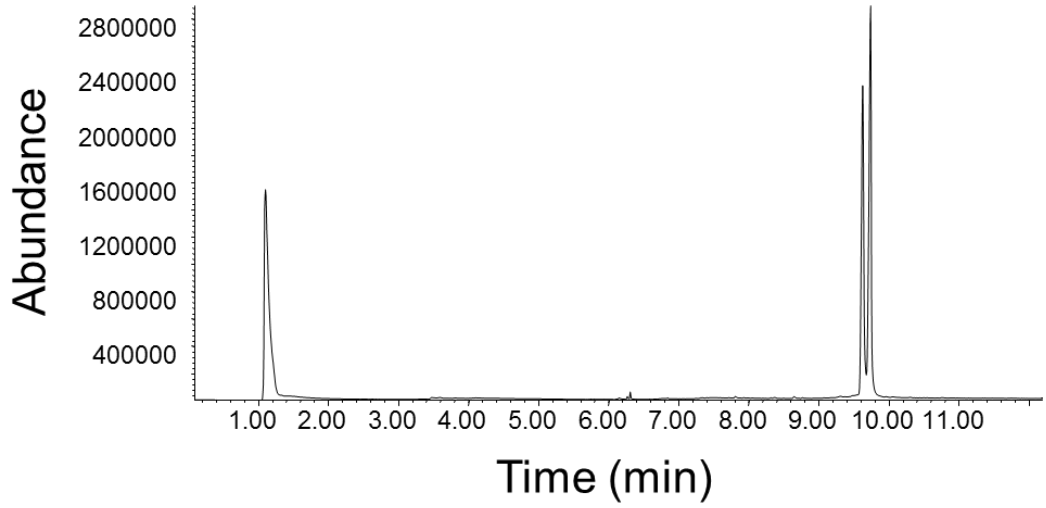

Fig. 3 TIC of fibers from the NyCo fabric with FF permethrin

Figure 4 shows a TIC of the Permethrin SFR concentrate before dilution with water. Other peaks in the chromatogram are due to petroleum distillates and triacetin, which are inactive ingredients but assist in emulsification of the permethrin.

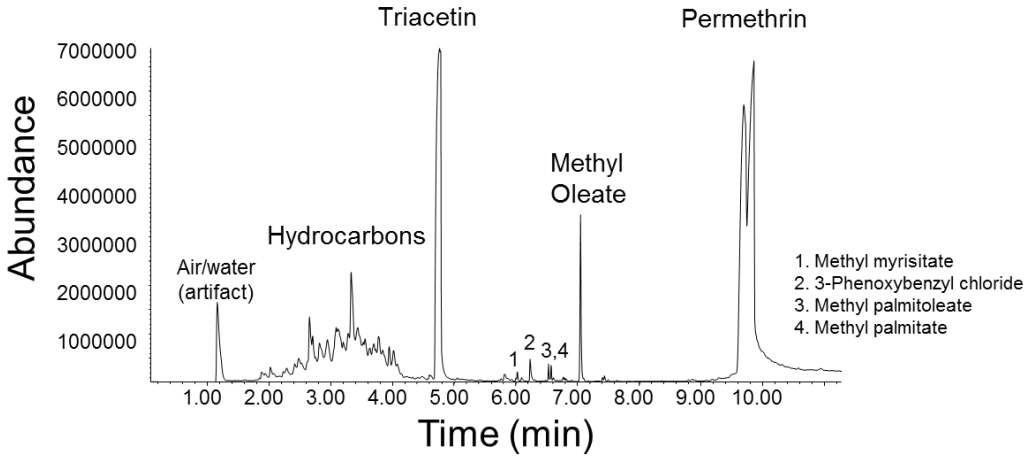

Fig. 4 TIC for Permethrin SFR concentrate with petroleum distillates (Martins)

4. Discussion

Since little material is required for D-GC-MS analysis, it is possible to analyze fibers pulled from different areas of the fabric and use the results to determine uniformity of the permethrin finish. Figure 5 shows the results of the testing for 3 different experiments (sample sets) using the FF NyCo: FF-1, FF-2, and FF-3.

Fabric was obtained from a whole garment, the ACU permethrin coat, and not from the factory roll goods. The history of the coat is not known, so it is possible that there was some wear, handling, and laundering, although the last condition is unlikely. If so, this would explain the lower than expected permethrin content, which according to the label would initially contain 0.52 wt % (±10%). Future work will focus on reproducibility studies and will include analysis of factory roll goods, if possible.

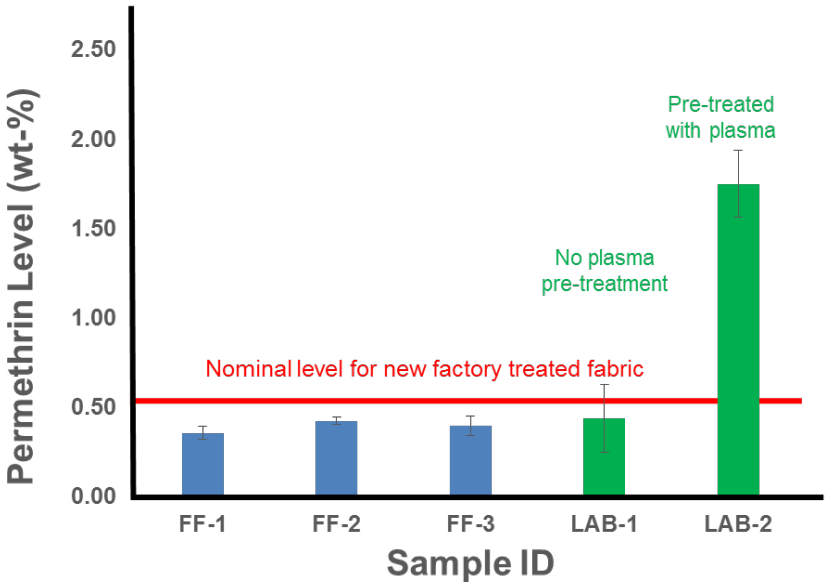

Fig. 5 Permethrin level (wt %) for as-received FF and laboratory-treated (LAB) fabrics as determined by D-GC-MS method

Although the overall permethrin content as determined by D-GC-MS is lower than that expected for new, factory roll fabric, the agreement between the 3 samples of FF specimens is quite good. This suggests that the method has excellent potential as a solvent-free analytical technique for permethrin on fabric and that the permethrin finish is quite uniform across the fabric specimen.

The LAB fabric samples tell a different story. Significantly different results were obtained for the 2 samples produced in the laboratory, LAB-1 and LAB-2. In addition, the error bars within each sample set are much larger than for the FF specimens. Note that one sample is pretreated with plasma, while the other is not. It is not clear at this time how this treatment could affect the permethrin level, as the substance was added directly to the fabric, and is not likely to have evaporated and had no opportunity to wash away. One possible explanation is that the plasma treatment itself, or perhaps the effect of the plasma treatment, was not uniform for some reason and that the permethrin tended to adhere more to some areas than others. More rigorous laboratory application methods would be necessary to

confirm if the higher level of permethrin is due to the presence of a plasma-treated surface or to other factors. Future work will include examination of the effect of the plasma pretreatment and will also focus on developing an application method that is more similar to the factory treatment. This will be done by saturating the garment in a contained environment with a known amount of permethrin in solution, followed by drying to remove all liquid.

5. Conclusions

A new method for determination of the level of permethrin on fabric has been developed and demonstrated for specimens from factory- and laboratory-treated uniform fabrics. It is expected that the method will be applicable to the analysis of other fabric treatments. Advantages of the new D-GC-MS method are that it is much quicker than the current standard method, and it is solvent-free and therefore greener and less costly than traditional solvent methods. The method is also useful for determining concentration distributions across a fabric specimen. This advantage may become a disadvantage in that only small samples can be examined in a given analysis, resulting in the need to analyze many samples to get representative values for concentration on a large specimen.

Analysis of plasma-treated fabric may indicate that it has a greater propensity to bond with permethrin than untreated fabric. Additional sample preparation and analysis would be necessary to confirm this.

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List of Symbols, Abbreviations, and Acronyms

AATCC	American Association of Textile Chemists and Colorists
ACU	Army Combat Uniform
D-GS-MS	desorption-gas chromatography–mass spectrometry
EPA	US Environmental Protection Agency
FF	factory-finished
LAB	laboratory-treated
NyCo	cotton and nylon
OCP	Operational Camouflage Pattern
RED	Reregistration Eligibility Decision
SIC	selected ion chromatogram
TIC	total ion chromatogram

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